

LCA Case Studies

Preliminary Assessment of the Environmental Benefits of Enzyme Bleaching for Pulp and Paper Making

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Abstract

Goal and Background. The LCA methodology is used to compare the potential environmental benefits of an emerging biotechnology, enzyme-bleaching, with those of elemental chlorine free (ECF) bleaching, an existing technology that is widely used in paper making. Through the use of biodegradable enzymes to supplement, or eventually to replace, chemicals in the bleaching process to extract lignin, enzyme bleaching processes are aimed to reduce the use of chlorine based bleaching chemicals and to achieve cost savings by circumventing investment into oxygen delignification or ozone bleaching technology.

Scope and Method. The assessment is conducted using SimaPro 4.0 and focuses on the processes within the bleach plant stage. For this study, ECF is replaced by enzyme bleaching only in the first stage of the bleaching process. Because this is a comparative study, all upstream and downstream processes are excluded. The impact categories based on Eco-indicator 95 are used to characterize the inventory data in this study. Other methodologies, such as Eco-indicator 99 and CML 2000, have not been chosen as they are more region-specific and are not yet fully applicable to the Canadian environmental condition. A new initiative to develop a Canadian Life Cycle Impact Assessment (LCIA) Method is ongoing at the Interuniversity Reference Center for the Life Cycle Assessment, Interpretation and Management of Products, Processes and Services (CIRAIG), Ecole Polytechnique, Canada.

Results and Conclusion. The analysis shows that the introduction of enzyme bleaching into the ECF process significantly improves the overall environmental performance in the majority of the impact categories. Extending the substitution of enzyme bleaching for chlorine dioxide is warranted. Of the three impact categories where increased impact was noted, two of these which increased emissions of greenhouse gases and increased incidence of summer smog, would be completely eliminated if the enzyme mediator was manufactured at the point of use. There remains a potential for increased impact from eutrophication, which would need to be managed.

Recommendations and Outlook. With the only partial substitution of ECF by enzyme bleaching examined here, chlorine dioxide consumption, energy consumption, NaOH consumption, and transportation remain the key hot spots and warrant further research. Anything that can be done to replace or reduce chlorine dioxide consumption will benefit the environment.

Keywords: Bio-bleaching; cellulose; elemental chlorine free (ECF) bleaching; enzyme bleaching; laccase; pulp and paper making; pulp bleaching; system closure

Introduction

While the making of paper has been known to exist for thousands of years, the processes involved have been continually refined through the course of the industrial age. With over 90% of paper products originating from wood, the wood must first be converted to pulp. The pulp then can either be dried and sold directly as market pulp, or can proceed through the paper machine to be transformed into paper.

For converting wood to pulp, there are many different manufacturing processes, ranging from mechanical processes to chemical processes, or as a combination of both. The principal pulping process is a chemical process known as the Kraft process (Encyclopedia of Chemical Technology, Paper [1]), whereby lignin and the hemicelluloses are largely dissolved out of the fiber matrix. The fibrous material obtained after digestion, consisting primarily of cellulose, is called pulp. Cellulose and hemicellulose are inherently white and do not contribute toward colour, while 'chromophoric groups' on the lignin are principally responsible for colour. Whereas the Kraft process cannot quantitatively eliminate lignin from the wood matrix, a bleaching treatment, therefore, is needed, since residual lignin and coloured extractives must be eliminated from the pulp for most uses, such as white paper. Moreover, complete removal of hemicelluloses also requires bleaching and purification. For recycled fiber, bleaching will help clear the pulp of resins, metallic ions and other substances coming from the used fiber.

As the goal of bleaching chemical pulp is the complete removal of lignin from the pulp, molecular chlorine (Cl_2) was used in traditional bleaching processes. Over the past ten years, however, Canadian producers have moved away from the traditional elemental chlorine to elemental chlorine-free (ECF) technology [2,3]. ECF, by definition, does not include the use of Cl_2 in bleaching, but does permit the use of ClO_2 . The use of chlorine dioxide can lead to the formation of Cl_2 as an intermediate. The peak of Cl_2 concentration during the ECF bleaching process, however, is almost a full order of magnitude lower than the peak Cl_2 concentration in the traditional chlorine bleaching sequence. This strategy results in significantly lower levels of organic chlorides, as measured by the AOX (adsorbable organic halides)

discharged from bleach plants. It also decreases the concentration of chlorine in the population of molecules, so that the toxicity and bioaccumulation of the pollutant is much less. Therefore, ECF has resulted in a dramatic improvement in the quality of pulp effluent by reducing the formation of organochlorines. However, it has also increased operating costs.

The enzyme bleaching process uses biodegradable enzyme to supplement, or eventually to replace, chemicals in the bleaching process for extracting the lignin. In Canada, about 10% of bleached Kraft pulp is now manufactured using xylanase (an enzyme) to reduce chlorine dioxide dosage. This application has already been found to be cost-effective. Current research on oxidative enzymes holds promise for greater chemical savings, and is compatible with system closure options, since it will not produce an effluent that is contaminated by chloride ion, and is therefore recyclable to the recovery system. The materials in the waste streams can be recovered, and there will be no detrimental impact on the mill environment.

Of possible oxidative enzyme candidates in pulp bleaching processes, laccase is probably of the greatest interest to the paper and pulp industry [4–7]. Laccase, classified as *benzenediol oxygen oxidoreductase*, belongs to a group of enzymes capable of oxidizing a wide range of phenolic and amine compounds. The range of substrates, and thus the applicability of laccases, can further be expanded by combining these enzymes with different mediators. Thus, substrates not naturally oxidized by laccases may be attacked through this mediated oxidation, thereby increasing the solubilization of lignin, and increasing the brightness of the pulp. The activity of laccase varies when combined with different mediators at different pH and buffer. Among the various laccase-mediator combinations tested in pulp mill conditions, laccase-NHA is found to be the most promising combination for delignification of Kraft pulps in mill applications [8].

There have been other Life Cycle Assessments, for example, conducted on pulp and paper processes [9]. The purpose of this study is to use the LCA methodology to compare the potential environmental impacts of enzyme-bleaching with those of an existing, widely-used-technology, elemental chlorine free (ECF) bleaching. The analysis also attempts to highlight those areas where further research or process design would be the most productive for improving the environmental performance of this technology.

1 Life Cycle Assessment

1.1 Method and scope

The assessment is conducted using SimaPro 4.0, and the impact categories based on Eco-indicator 95 are used to characterize the inventory data in this study. Other methodologies, such as Eco-indicator 99 and CML 2000, have not been chosen as they are more region-specific and not yet fully applicable to the Canadian environmental condition. A new initiative to develop a Canadian Life Cycle Impact Assessment (LCIA) Method is ongoing at the Interuniversity Reference Center for the Life Cycle Assessment, Interpretation and Management of Products, Processes and Services (CIRAIG), Ecole Polytechnique, Canada, but results from this effort are not yet available.

1.2 System boundary

The study focuses only on the environmental performance of the bleach plant. All other processes are excluded from the study. Within the bleach plant, the study encompasses all the processes and their inputs, such as chemicals, energy and fuel, the production of the inputs, transportation of the materials, and all the emissions generated. The environmental influences caused by the production of capital equipment and facilities used in the bleach plant are not included.

According to Paprican, over 76% of Canadian bleached Kraft production uses the ECF process. The process usually involves repeated applications of the two stages: a chlorine dioxide stage and an alkaline extraction stage. These are carried out in sequence with washings in between. The ECF process most commonly used for softwood pulps includes the sequence:

unbleached pulp → D₀ (zero chlorine dioxide bleaching stage) → E_O (alkaline extraction stage with oxygen added under pressure for the first part of the stage) → D₁ (first chlorine dioxide bleaching stage) → E_P (alkaline extraction stage with hydrogen peroxide added) → D₂ (second chlorine dioxide bleaching stage) → bleached pulp, without oxygen delignification (Fig. 1). The notation, based on the chemicals, is explained in Table 1. This process has been chosen as the reference process for this study, against which the performance of enzyme bleaching is compared.

The corresponding sequence for the newly developed enzyme bleaching process is: unbleached pulp → L (enzyme bleaching stage with mediator added) → E_O → D₁ → E_P → D₂ → bleached pulp, where the D₀ stage in the ECF process

Table 1: Chemicals used in bleaching process [1]

Notation	Name	Formula	Form used	Lignin function
D	Chlorine dioxide	ClO ₂	7–10 g/l (aq)	Oxidize, brighten and solubilize
O	Oxygen	O ₂	Gas, used with NaOH	Oxidize and solubilize
P	Hydrogen peroxide	H ₂ O ₂	2–5 wt% (aq)	Oxidize and brighten
E	Sodium hydroxide	NaOH	5–10 wt% (aq)	Solubilize and hydrolyze chlorolignin

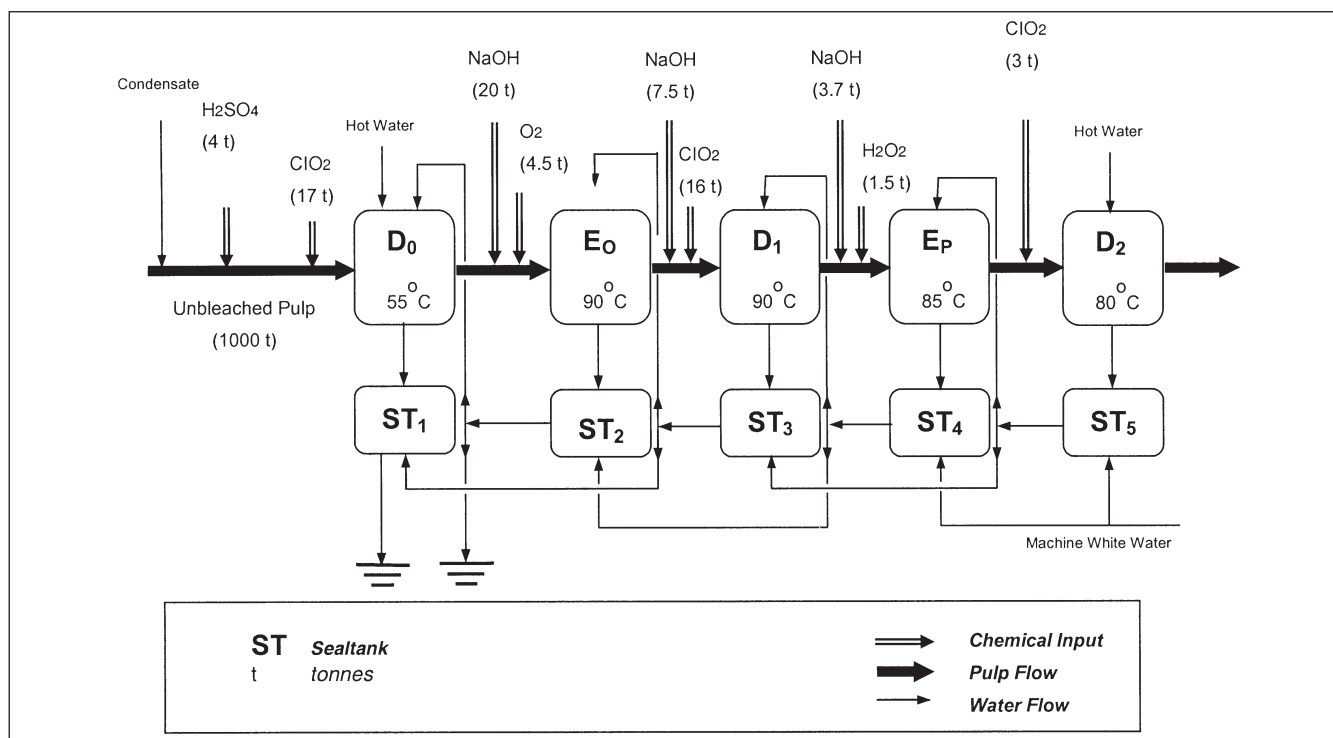


Fig. 1: The ECF process

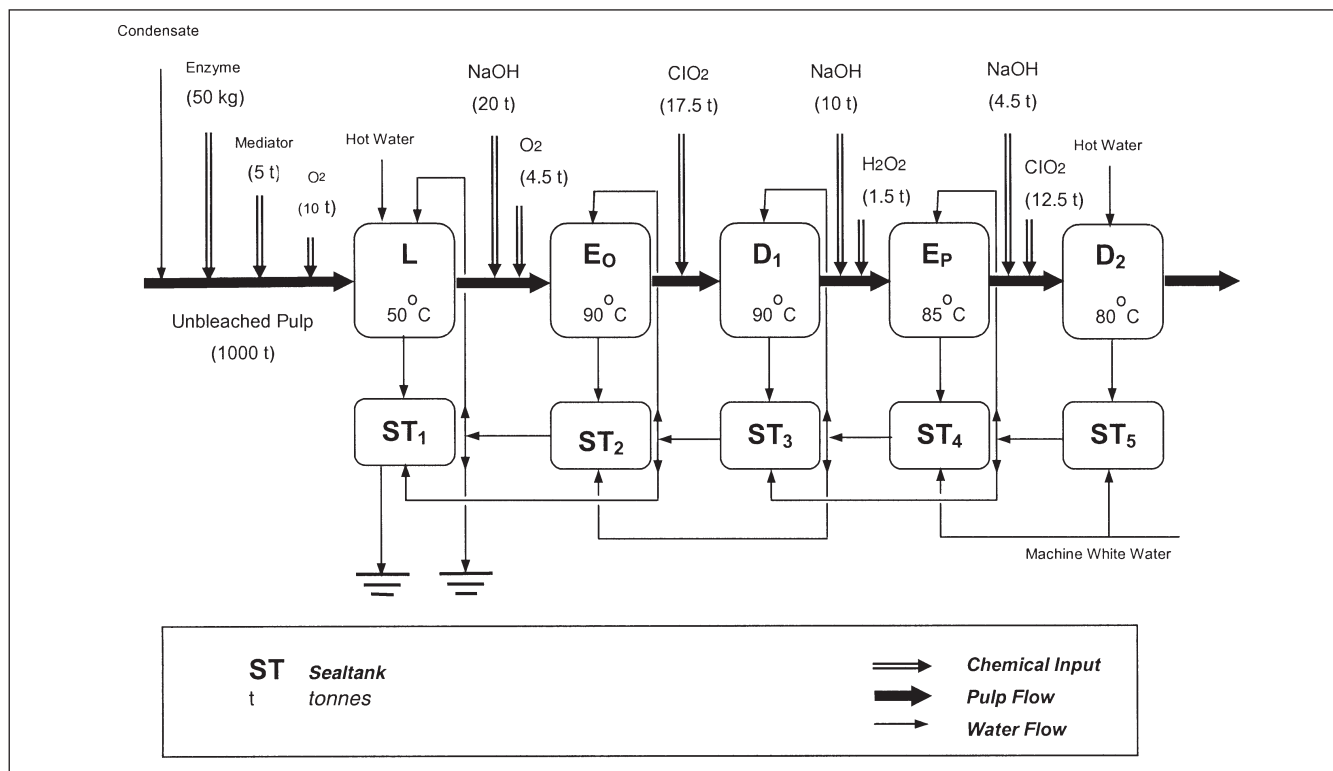


Fig. 2: The enzyme bleaching process

has been replaced by the L stage (Fig. 2). The processes in all the other stages are the same, except for different chemical consumptions and pH conditions.

Allocation in this study is done on a mass basis.

1.3 Functional unit

In this study, the Functional Unit is defined as the production of one moisture-free metric ton of bleached pulp in a Canadian context using specific pulping scenarios. The

bleached pulps in the two scenarios, ECF bleaching and enzyme bleaching, are assumed to have the same physical and chemical properties, such as strength, brightness, etc.

1.4 Data collection

The primary data for ECF bleaching, such as direct chemical inputs and emissions, were provided by Paprican. The data represents the average performance of a Canadian ECF bleaching plant. When a range is provided, the average value is used. For the enzyme bleaching process, because the technology is still under development in the laboratory and the process is not yet utilized in an existing plant, site-specific data is not available. Laboratory averages are therefore used in this case.

Information on the production of the chemical inputs was obtained from different sources, including individual manufacturers, literature, and the SimaPro database. Attempts have been made to ensure the data used correctly reflects today's technology. However, there are some data gaps due to confidentiality or uncertainty. These data gaps are filled using assumptions noted below and their significance is assessed through sensitivity analysis.

Energy sources in this study are taken from the average energy sources for the Canadian pulp and paper industry in 1995, as shown in Table 2. The form of energy supply in pulp mills is some steam and mostly electricity. Electricity-to-steam ratios for a conventional backpressure steam turbine are roughly 60 kWh/GJ with no intermediate extraction, and about 40 kWh/GJ with intermediate extraction [10].

Table 2: 1995 annual energy demand by source in Canadian pulp and paper mills

Source	Petajoules (10^{15} joules)	Percent (%)
Refined petroleum products	64.2	7.3
Electricity	189.6	21.5
Natural gas	128.1	14.5
Other fuels	8.4	1.0
Wood waste	141.5	16.1
Spent pulping liquor	349.1	39.6
Total	881.0	100.0

Electricity used in a bleaching plant is primarily used for chemical mixing and pumping stock and filtrate. For the five-stage D-Eo-D-Ep-D sequence, electrical demand for each stage is in the order of 20–30 kWh/adt (adt means air dry ton). The chemicals used in bleaching are generally produced off-site. The energy required to produce them is not accounted for in the mill's energy balance. Table 3 summarizes the electrical energy required to produce a number of bleach plant chemicals [10].

The steam consumption at each stage in this study has been estimated based on the average working temperatures for

Table 3: Electrical energy needed for producing bleach plant chemicals [10]

Chemicals	KWh/kg
Chlorine dioxide (ClO_2) ^(b)	9.25
Sodium hydroxide (NaOH)	2.8
Sodium chlorate (NaClO_3)	5.6
Sulphuric acid (H_2SO_4)	0.1
Methanol (CH_3OH)	0.06
Oxygen (O_2)-cryogenic	1.15
Oxygen (O_2)-PSA/VSA	0.4
Hydrogen peroxide (H_2O_2)	0.75

^(b) Based on R8 generator

each stage as shown in Fig. 1. It is for compensating the heat loss at the towers and washers, and for warming up the water and pulp mixture to working temperature between stages. The average steam consumption in a bleaching plant for North American softwood mills designed during the 1990s is about 0.58 GJ/adt [10].

1.5 Key assumptions

- All the transportation considered in the study, except for the mediator, is assumed to be by road using medium-heavy diesel trucks with an average load range of 6.4–15 tons. The transportation distance is assumed to be 200 km (400 km, two ways).
- The mediator is assumed to be transported by air from Germany (where it is produced) to Canada first, and then by diesel truck from the airport to the mill. The distance for air travel is estimated to be 8,000 km (one way). Road transportation is assumed to be 20 km (40 km, two ways).
- Chlorine dioxide is assumed to be produced on-site using an R8/R10 generator, which accounts for 89% of the chlorine dioxide produced in Canadian mills [11]. It is generated by the reaction of sodium chlorate with methanol as the reducing agent.
- For the electricity generated by spent pulping liquor, the weak black liquor from the brown stock has to pass through liquor concentration in an evaporator before it can be burned efficiently in the recovery furnace to recover the energy. The energy consumption and emissions associated with the evaporator and recovery furnace should be included in the accounting of impact. While it is debatable what proportion should be allocated, this case study assumes a 100% allocation. The heating value of lignin is assumed to be the same as that from rice straw – 11,783 BTU/lb.
- The size and shape of the tower and washer in each stage, and the heat transfer coefficient is assumed to be the same. The room temperature is assumed to be 18°C. The initial temperature of the make-up water is assumed to be taken from underground water with an assumed temperature of 10°C. The consistency of the flow is assumed to be 12%.

- Sodium sulfate is assumed to be solid waste for disposal.
- Inventory data associated with enzyme manufacturing are taken from 1997 environmental data published <http://www.novo.dk/vironm/abr98/grafer/Site/site_35_1.html> on the Novo Nordisk Franklinton U.S.A site. Raw materials are assumed to be cultivated in the same way as hay. Salt nutrients were ignored in hay production. Inventory data, except raw material consumption associated with pesticide manufacturing, are taken from the 1998 Novartis environmental report <<http://www.info.novartis.com/media/main.html>>.
- Some studies have reported that enzyme bleaching may lead to a yield reduction, necessitating more wood per ton of pulp produced. However, our source for this study did not indicate that this had occurred.

Due to a lack of data sources, the following assumptions were made on the existing data gaps in the study:

- No environmental impact is associated with mediator manufacturing. There has been some suggestion that the use of a mediator is potentially toxic due to mediator characteristics or the existence of toxic intermediates associated with the production process. However, it is not possible to take this into account in this study due to data which has not been available.
- No emissions are associated with cryogenic oxygen production.
- No raw material consumption is associated with H₂O₂ manufacturing.
- For energy production by wood waste, no environmental impact is associated with obtaining wood wastes.
- No raw material consumption and emissions are associated with methanol manufacturing.
- No emission is associated with the evaporator operation.
- No emission is associated with the recovery furnace, but VOCs are accounted for.

For the following processes, European data are used:

- Per distance emissions and fuel consumption associated with road transportation (SimaPro 4.0, Truck I, source IDEMAT 96).
- Per distance emissions and fuel consumption associated with air transport (SimaPro 4.0, IDEMAT 96).
- The types of fuel used are taken from the average energy sources for the Canadian pulp and paper industry. However, inventory data for the energy production by each fuel type are taken from European data (SimaPro 4.0, *electricity from coal B250, electricity from oil B250, electricity from gas B250, electricity from uranium B250, electricity from hydropower B250, and electricity from lignite B250*).
- Inventory data associated with sulfuric acid manufacturing are derived from Lurgi 1995 (SimaPro 4.0, Sulfuric acid B250, BUWAL 250).
- Inventory data associated with NaOH manufacturing are 1998 average, western European (SimaPro 4.0, NaOH P 1998).

2 Results and Discussions

In Fig. 3, the environmental performance of enzyme bleaching is compared with that of traditional ECF bleaching under ten impact categories built into the SimaPro methodology. Fig. 3 indicates that, compared with ECF bleaching, partial replacement by enzyme bleaching produces fewer ozone depleting substances, fewer acidifying emissions, fewer heavy metals, fewer carcinogenic substances, fewer winter smog emissions and fewer solid wastes, and consumes less energy. However, it gives off more greenhouse gases, causes more summer smog, and more eutrophication. The emissions of more greenhouse gases and more summer smog are mainly due to the transportation of mediator by international flights, while eutrophication is mainly caused by enzyme manufacturing and feedstock cultivation.

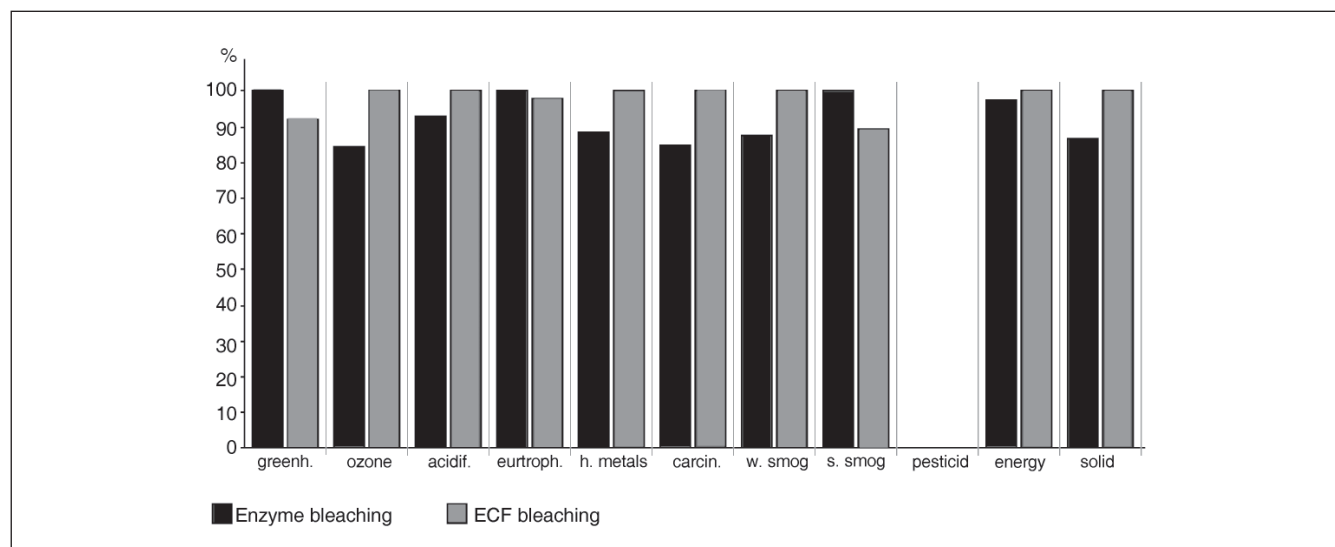


Fig. 3: Comparison of environmental impacts from enzyme bleaching process and traditional ECF bleaching process

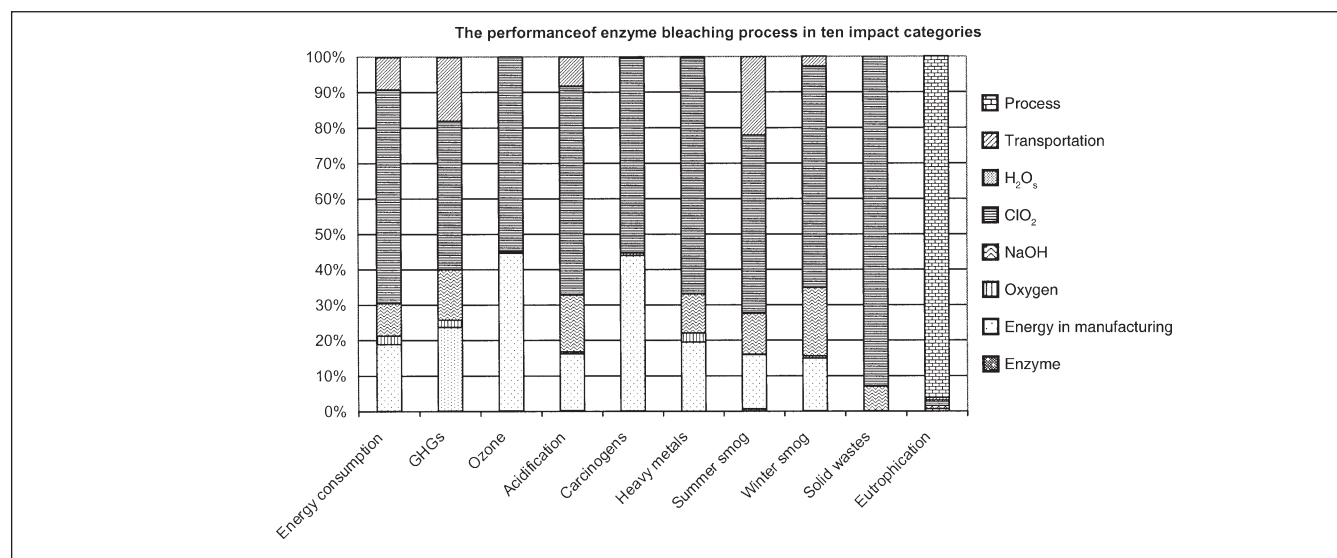


Fig. 4: The distribution of the environmental performance, in characterization result, in terms of resource consumption

Fig. 4 shows the distribution of the environmental performance of enzyme bleaching in terms of resource consumption. Chlorine dioxide use is the largest energy consumer followed by energy production and transportation. This is due to the fact that the chlorine dioxide manufacturing is energy-intensive, and that the chlorine dioxide is used in large quantities. The energy consumption attributed to energy production is due to the fact that the extraction and the processing of the fuel are energy consuming. The energy consumption attributed to transportation is mainly due to the shipment of the mediator by air from Germany to the point of use in Canada.

For greenhouse gas emissions, the carbon dioxide emissions presented in this study are only those derived from fossil sources. The bio-based carbon dioxide emission is treated as zero. Most of the greenhouse gas emissions in partial enzyme bleaching are still due to the energy consumption for producing NaClO_3 and chlorine dioxide. The emissions attributed to transportation are mainly due to the transportation of mediator by international flight. The NaOH manufacturing process also results in a relatively large amount of carbon dioxide emissions.

For ozone depleting substances, the emissions caused by chlorine dioxide consumption are due to the energy consumed in its production. The ozone depleting gas Halon-1301 is emitted during energy production processes from coal, lignite, oil, gas, or even uranium.

Acidifying substances include NO_x , SO_2 , HCl, etc. The most acidifying emissions in enzyme bleaching come from the consumption of chlorine dioxide. Sulfuric acid and NaClO_3 are needed as raw materials for chlorine dioxide production. The production of sulfuric acid and NaClO_3 emits HCl air emissions. Acidifying emissions from energy production are mainly SO_x as acidifying gases from the production process. Transportation emits NO_x , while NaOH manufacturing emits SO_x , NO_x and HCl gases in its process.

For carcinogenic substances, the emissions caused by chlorine dioxide consumption are mainly due to the energy consumption in its production. Energy production emits PAHs, Ni, and other carcinogenic air emissions.

For heavy metals, the emissions caused by chlorine dioxide consumption are mainly due to the energy consumed in its production. Energy production emits heavy metals including Pb, Cr, As, Ba, etc.

The summer smog emissions caused by chlorine dioxide consumption are mainly due to NaCl production, and partly due to the energy consumption for NaClO_3 production. The emissions caused by NaOH manufacturing are mainly due to hydrocarbons (C_xH_y) emissions from its manufacturing processes.

Winter smog is the total mass of SO_2 emission and dust (SPM) emission. They are mostly a result of the consumption of chlorine dioxide, and to a lesser extent from energy production and NaOH manufacturing. Chlorine dioxide manufacturing needs sulfuric acid for the production, while sulfuric acid production emits SO_x emission. Energy production also results in SO_x emission. NaOH manufacturing emits SO_x and SPM emissions during its production processes.

Solid wastes are the result of the consumption of chlorine dioxide, the production of which generates sodium sulfate as a by-product. Sodium sulfate, however, can be used in the Kraft pulping liquor to provide make-up sodium and sulfur. In this study, the worst-case scenario, where sodium sulfate is treated as a waste, is assumed.

Eutrophication is caused by the addition of organic material, nitrogen and phosphorus. The largest volume of emissions comes from the process itself, and decreases as the pulp flows from one stage to another.

Fig. 5 shows the distribution of the environmental performance of enzyme bleaching between different stages. The overall order of significance of its performance between stages, except for eutrophication, can be summarized as: $D_1 > D_2 > E_O > E_P > L$. This is perhaps due to the joint effects of cooking temperature and chlorine dioxide consumption in the different stages. The order of significance for eutrophication emissions is: $L > E_O > D_1 > E_P > D_2$. This is because the remaining lignin and other organic materials that can be extracted from the pulp will decrease as the pulp passes from the first stage (L) to the last (D_2).

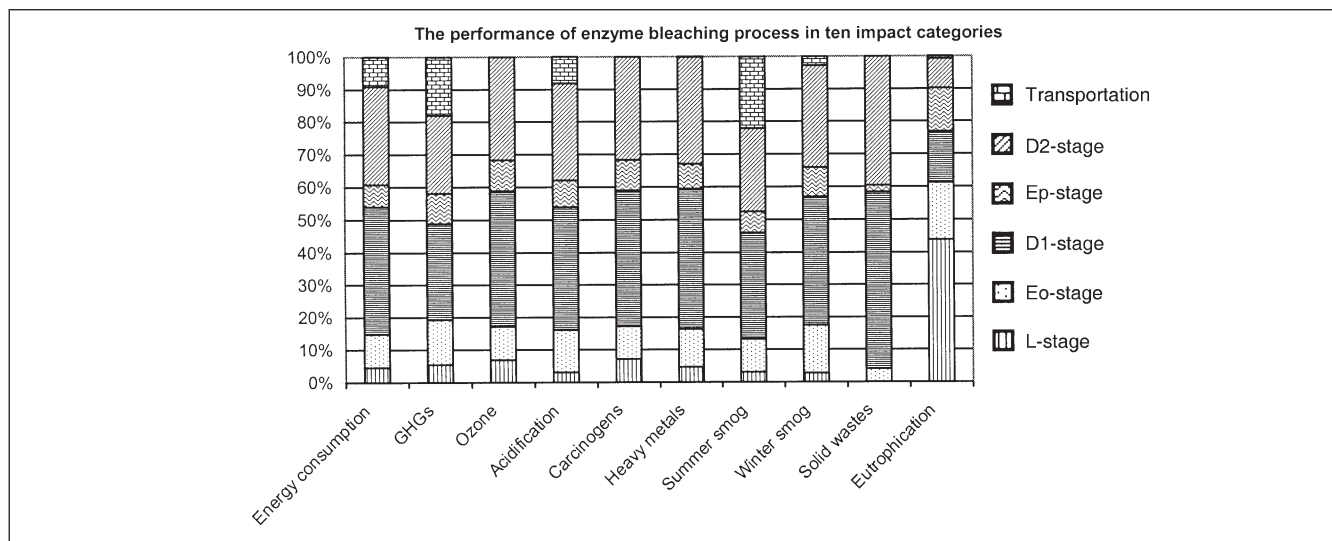


Fig. 5: The distribution of the environmental performance, in characterization result, between stages

3 Conclusions

The following conclusions are drawn from the study:

- Further substitution of the ECF bleaching process with the enzyme bleaching process has the potential to save energy, cause less acidification, discharge fewer ozone depleting substances and fewer heavy metals, fewer carcinogenic substances, less winter smog, and fewer solid wastes. It can, however, give off more greenhouse gases, more summer smog and more eutrophying emissions if the enzyme is produced far from the point of use.
- The magnitude of emissions for each stage in enzyme bleaching processes for all impact categories, except eutrophication, can be described by: $D_1 > D_2 > E_O > E_P > L$.
- Chlorine dioxide consumption, energy consumption, NaOH consumption, and transportation are the main hot spots in enzyme bleaching, while the biggest polluter is still chlorine dioxide. This means that anything that can be done to replace or reduce chlorine dioxide consumption will benefit the environment.

Whether the enzyme bleaching process or the ECF bleaching process is cleaner is sensitive to the choice of energy production, mediator transportation, NaOH manufacturing, and the accuracy of the primary data. The conclusion, however, is not sensitive to chlorine dioxide manufacturing, road transportation, or hydrogen peroxide manufacturing.

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